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AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH,  
CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI,  
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For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

(54) Title: SILICA

(57) Abstract: Silanised, structurally modified, pyrogenically produced silicas, characterised by groups fixed to the surface, wherein the groups are dimethylsilyl and/or monomethylsilyl, are produced in that pyrogenically produced silica is treated by a known method with dimethyldichlorosilane and/or monomethyltrichlorosilane, the groups dimethylsilyl and/or monomethylsilyl being fixed on the surface of the pyrogenic silica, and is then structurally modified and optionally post-ground. They are used to improve scratch resistance in lacquers.

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## Silica

The invention relates to a silanised, structurally modified, pyrogenically produced silica, a process for the production thereof and its use.

- 5 It is known to use nanoscale particles in transparent coating compositions.

Thus, according to US 6,020,419, pyrogenically produced silicon dioxides, deagglomerated *in situ*, which have been made hydrophobic with dimethyldichlorosilane (Aerosil® R  
10 972), are used in polyurethane lacquers to improve the scratch resistance of the coatings.

The known silica has the disadvantage that it cannot be produced in powder form without a lacquer binder.

- 15 The object therefore existed of developing a silica that does not have these disadvantages.

The present invention provides silanised, structurally modified, pyrogenically produced silicas, which are characterised by groups fixed on the surface, the groups  
20 being dimethylsilyl and/or monomethylsilyl, preferably dimethylsilyl.

In a preferred embodiment of the invention the silicas can have the following physico-chemical characteristics:

BET surface area m <sup>2</sup> /g:	25 - 400
Average size of the primary particles nm:	5 - 50
pH value:	3 - 10
Carbon content %:	0.1 - 10
DBP value %:	< 200

- 25 The silica according to the invention can have a tamped density of 100 to 280, preferably 100 to 240 g/l.

A tamped density of more than 280 g/l leads to poorer results in the technical lacquer tests.

Pyrogenic silicas are known from Winnacker-Küchler  
Chemische Technologie, volume 3 (1983)

- 5 4th edition, page 77 and  
Ullmanns Enzyklopädie der technischen Chemie, 4<sup>th</sup> edition  
(1982), volume 21, page 462.

- In particular, pyrogenic silicas are produced by flame  
hydrolysis of vaporisable silicon compounds, such as e.g.  
10  $\text{SiCl}_4$ , or organic silicon compounds, such as  
trichloromethylsilane.

- The invention also provides a process for the production of  
the silanised, structurally modified, pyrogenically  
produced silicas according to the invention, which is  
15 characterised in that pyrogenically produced silica is  
treated with dimethyldichlorosilane and/or  
monomethyltrichlorosilane by a known method, the  
dimethylsilyl and/or monomethylsilyl groups being fixed on  
the surface of the pyrogenic silica, and is then  
20 structurally modified and optionally post-ground.

In one embodiment of the invention a tempering can take  
place after the structural modification and/or post-  
grinding.

- The silicas according to the invention can be produced e.g.  
25 as follows:

- The silicas, which can be produced as described in DE 1 163  
784, are then structurally modified by mechanical action  
and possibly post-ground in a mill. A tempering can  
possibly take place after the structural modification  
30 and/or post-grinding.

The structural modification can take place e.g. with a ball  
mill or a continuously operating ball mill. The post-

grinding can take place e.g. using an air-jet mill or pin mill. The tempering can take place batchwise, e.g. in a drying cupboard, or continuously, e.g. in a fluidised bed. The tempering can take place under protective gas, e.g. nitrogen.

5

The silicas according to the invention can be incorporated into lacquers, as a result of which these lacquers have increased scratch resistance.

ExamplesProduction and physico-chemical properties of the silicas

Production of the comparative silicas:

- 5 The production of the comparative silicas 1, 2 and 3 takes place as described in DE 1 163 784.

Production of the silicas according to the invention:

- The silicas, which are produced as described in DE 1 163 784, are then structurally modified by mechanical action  
10 and possibly post-ground in a mill. A tempering can possibly take place after the structural modification and/or post-grinding.

- The structural modification can take place e.g. with a ball mill or a continuously operating ball mill. The post-  
15 grinding can take place e.g. using an air-jet mill or pin mill. The tempering can take place batchwise, e.g. in a drying cupboard, or continuously, e.g. in a fluidised bed. The tempering can take place under protective gas, e.g. nitrogen.

**Table 1:** Overview of the production of the comparative silicas and the silicas according to the invention (Examples)

Designation	Surface-fixed group	Structural modification	Post-grinding after structural modification	Tamping after post-grinding
Comparative silica 1	Dimethylsilyl	No	-	-
Comparative silica 2	Dimethylsilyl	No	-	-
Comparative silica 3	Dimethylsilyl	No	-	-
Silica 1	Dimethylsilyl	Yes	No	No
Silica 2	Dimethylsilyl	Yes	No	No
Silica 3	Dimethylsilyl	Yes	No	No
Silica 4	Dimethylsilyl	Yes	No	No
Silica 5	Dimethylsilyl	Yes	Yes	No
Silica 6	Dimethylsilyl	Yes	No	No
Silica 7	Dimethylsilyl	Yes	Yes	No
Silica 8	Dimethylsilyl	Yes	Yes	Yes
Silica 9	Dimethylsilyl	Yes	Yes	Yes
Silica 10	Dimethylsilyl	Yes	Yes	No
Silica 11	Dimethylsilyl	Yes	Yes	No

**Table 2:**Physico-chemical data of the silicas according to the invention (Examples) and the comparative silicas

Designation	Tamped density [g/L]	Loss on drying [%]	Loss on ignition [%]	pH value	C content [%]	DEP adsorption [%]	BET specific surface area [m <sup>2</sup> /g]
Comparative silica 1	64	0.1	0.5	4.0	0.8	243	113
Comparative silica 2	67	0.5	0.6	4.8	1.0	256	165
Comparative silica 3	72	0.7	1.0	4.0	1.6	255	256
Silica 1	236	0.1	0.6	4.0	0.8	127	115
Silica 2	204	0.1	0.6	3.9	0.8	137	116
Silica 3	223	0.3	0.7	4.2	1.0	160	169
Silica 4	186	0.3	0.7	4.2	1.1	152	171
Silica 5	109	0.2	0.7	4.4	1.1	159	167
Silica 6	193	1.2	0.7	5.2	1.7	157	258
Silica 7	125	0.2	0.7	4.1	0.8	130	110
Silica 8	108	0.7	1.3	5.0	1.7	156	257
Silica 9	123	0.3	0.5	4.3	1.1	157	165
Silica 10	102	0.7	1.2	6.2	1.7	164	256
Silica 11	160	0.2	0.7	4.0	0.8	132	115

Example 1:

For the investigation of the improvement in scratch resistance, a conventional 2-component polyurethane lacquer was used. The formulation of the lacquer and its production, including application, are summarised below:

## Formulation

Millbase	Parts by wt.
Acrylic copolymer, mod. with synthetic fatty acids, 60% solution	43.4
Butyl acetate 98%	17.8
Xylene	3.9
AEROSIL	5.0
$\Sigma$	70.7
Lacquer make-up	
Xylene	11.3
Ethoxypropyl acetate	3.4
Butyl glycol acetate	1.6
Aliphatic polyisocyanate, approx. 75% in 1-methoxypropyl-2-acetate/xylene 1:1	18.6
$\Sigma$	105.0



Binder concentration: 40%

AEROSIL calculated on the basis of millbase (solids): 19.2%

AEROSIL calculated on the basis of lacquer (total): 5.0%

AEROSIL calculated on the basis of lacquer (solids): 12.5%

#### Production and application of the lacquers

The binder is mixed with the solvents. Then, for the purpose of predispersion, the AEROSIL is incorporated into this mixture with the high-speed mixer (disk Ø 45 mm) and predispersed for 5 min at 2000 rpm. The mixture is dispersed in a laboratory pearl mill for 30 min at 2500 rpm and 60% pump capacity using glass beads (Ø approx. 1 mm). The millbase is tested with a grindometer, 25 µm, in accordance with DIN ISO 1524. It must be smaller than 10 µm.

The conversion of the millbase to lacquer takes place in accordance with the formulation, the components being mixed with a vane agitator at 2000 rpm. The hardener is incorporated in the same way.

After adjusting the lacquers to spray viscosity in accordance with DIN 53411, the lacquers are applied to black lacquered metal sheets, e.g. DT 36 (from Q-Panel), by spray application (coat thickness about 40-50 µm). After spraying, the metal sheets are dried for 24 h at room temperature and then for 2 h in a drying oven at 70°C.

#### Scratch tests:

The metal sheets are abraded with a quartz/water slurry (100 g water + 1 g Marlon A 350, 0.25% + 5 g Sikron F500) using an abrasion and washing resistance tester (Erichsen, brush with hog's bristles). The gloss before and 10 min after the abrading is determined with a reflectometer (20° irradiation angle).

**Table 3:** Summary of the properties of the liquid lacquers relevant in terms of lacquer technology, and of the applied and dried films.

	Comparative silica 1	Silica 1	Silica 2	Reference	Comparative silica 2	Silica 3	Silica 4	Reference
Grindometer value [ $\mu\text{m}$ ]	< 10	< 10	< 10	/	< 10	< 10	< 10	/
Viscosity (millbase) [mPas]								
6 rpm	4710	421	772	571	4990	802	772	55
60 rpm	1120	210	264	225	1200	279	264	52
Viscosity (lacquer + hardener) [mPas]								
6 rpm	882	105	210	135	857	235	105	70
60 rpm	239	75	92	79	242	100	26	37
Flow	Orange-peel	OK	OK	OK	Orange-peel	OK	OK	OK
Scratch resistance								
20° reflectometer value before scratching	39.0	83.4	83.5	88.8	67.2	84.2	82.6	89.3
Haze before scratching	430	30	40	3	235	18	10	2
40 strokes with Sikron F 500 residual gloss [%]	/	83.7	82.3	56.0	/	74.7	80.4	47.2

The silicas 1 + 2 and 3 + 4 according to the invention can be used in high concentrations without impairing the appearance of the lacquer surface owing to their substantially lower rheological efficiency compared with comparative silicas 1 and 2. In addition, the silicas according to the invention display a substantial improvement in the scratch resistance of the lacquer surface.

Example 2

In this example the influence of the structural modification was investigated on the basis of a high solids 2-component PU clear lacquer. The formulation of the lacquer and its production, including application and testing, are summarised below:

Formulation

Millbase	Parts by wt.
Acrylic copolymer, mod. with synthetic fatty acids, 70% in n-butyl acetate	61.0
Butyl acetate 98%	7.3
Methoxypropyl acetate	1.7
Solvesso 100	2.0
Xylene	2.0
Baysilon OL 17, 10% in xylene (silicone oil)	0.7
AEROSIL	5.0
$\Sigma$	79.7
Lacquer make-up (hardener)	
Aliphatic polyisocyanate, 90% in n-butyl acetate	22.3
Butyl acetate 98%	2.0
Solvesso 100	1.0
$\Sigma$	105.0

Binder concentration: 62.8%  
Aerosil calculated on the basis of millbase (solids): 11.7%  
Aerosil calculated on the basis of lacquer (total): 5.0%  
Aerosil calculated on the basis of lacquer (solids): 8.0%

5

#### Production and application of the lacquers

The binder is mixed with the solvents. Then, for the purpose of predispersion, the AEROSIL is incorporated into this mixture with the high-speed mixer (disk Ø 45 mm) and predispersed for 5 min at 2000 rpm. The mixture is dispersed in a laboratory pearl mill for 30 min at 2500 rpm and 60% pump capacity using glass beads (Ø approx. 1 mm). The millbase is tested with a grindometer, 25 µm, in accordance with DIN ISO 1524. It must be smaller than 10 µm.

The conversion of the millbase to lacquer takes place in accordance with the formulation, the components being mixed with a vane agitator at 2000 rpm. The hardener is incorporated in the same way.

After adjusting the lacquers to spray viscosity in accordance with DIN 53411, the lacquers are applied to black lacquered metal sheets, e.g. DT 36 (from Q-Panel), by spray application (coat thickness about 40-50 µm). After spraying, the metal sheets are dried for 24 h at room temperature and then for 2 h in a drying oven at 70°C.

Scratch tests:

The metal sheets are abraded with a quartz/water slurry (100 g water + 1 g Marlon A 350, 0.25% + 5 g Sikron F500) using an abrasion and washing resistance tester (Erichsen, brush with hog's bristles). The gloss before and 10 min after the abrading is determined with a reflectometer (20° irradiation angle).

Table 4: Summary of the properties of the liquid lacquers relevant in terms of lacquer technology, and of the applied and dried films.

	Comparative silica 2	Silica 3	Silica 4	Reference
Grindometer value      [ $\mu\text{m}$ ]	< 10	< 10	< 10	/
Viscosity (millbase) [mPas]				
6 rpm	6200	1500	541	140
60 rpm	2100	900	559	195
Viscosity (lacquer + hardener) [mPas]				
6 rpm	3821	1041	497	167
60 rpm	1320	666	446	195
Flow	marked orange-peel	OK	OK	OK
20° reflectometer value before scratching	81.0	83.5	82.8	88.0
Haze	25	5	6	2
40 strokes with Sikron F 500 residual gloss      [%]		94.3	93.4	82.0

The silicas 3 + 4 according to the invention can be used in high concentrations without impairing the appearance of the lacquer surface owing to their substantially lower

rheological efficiency compared with comparative silica 2. In addition, the silicas according to the invention display a substantial improvement in the scratch resistance of the lacquer surface.

Example 3

Direct comparison of the silicas according to the invention with a scratch-resistant lacquer according to DE 198 11 790 A1, in which AEROSIL R 972 is used to improve the scratch

5 resistance.

	Prior art 1)	Silicas 2) according to the invention
Millbase		
Desmophen A 2009/1		190.2
Methoxypropyl acetate : Solvesso 100 1:1		36.8
AEROSIL		23.0
$\Sigma$		250.0

Lacquer make-up		
Desmophen A YEP4-55A, contains AEROSIL R 972	96.0	-
Millbase	-	48.9
Desmophen 2009/1	-	24.9
OL 17, 10% in MPA	-	-
Modaflow 1% in MPA	-	-
MPA : Solvesso 100 1:1	11.6	33.8
Butyl glycol acetate	10.5	10.5
Byketol OK	7.5	7.5
Byk 141	0.8	0.8

Hardener addition		
Desmodur N 3390	23.6	23.6
$\Sigma$	150.0	150.0



Production and application of the lacquers

- 1) Comparative silica 1 is incorporated into the binder in accordance with DE 198 11 790 A1 using a jet disperser.
- 5 2) The binder is mixed with the solvents. Then, for the purpose of predispersion, the AEROSIL is incorporated into this mixture with the high-speed mixer (disk Ø 45 mm) and predispersed for 5 min at 2000 rpm. The mixture is dispersed in a laboratory pearl mill for  
10 30 min at 2500 rpm and 60% pump capacity using glass beads (Ø approx. 1 mm). The millbase is tested with a grindometer, 25 µm, according to DIN ISO 1524. It must be smaller than 10 µm.

The conversion to lacquer of the millbases corresponding to  
15 1) or 2) takes place in accordance with the formulation, the components being mixed at 2000 rpm with a vane agitator. The hardener is incorporated in the same way.

After adjusting the lacquers to spray viscosity in accordance with DIN 53411, the lacquers are applied to  
20 black lacquered metal sheets, e.g. DT 36 (from Q-Panel), by spray application (coat thickness about 40-50 µm). After spraying, the metal sheets are dried for 24 h at room temperature and then for 2 h in a drying oven at 70°C.

Scratch tests:

The metal sheets are abraded with a quartz/water slurry (100 g water + 1 g Marlon A 350, 0.25% + 5 g Sikron F 500) using an abrasion and washing resistance tester (Erichsen, brush with hog's bristles). The gloss before and 10 min after the abrading is determined with a reflectometer (20° irradiation angle).

Table 5: Summary of the properties of the liquid lacquers relevant in terms of lacquer technology, and of the applied and dried films.

	Prior art	Silica 1	Silica 4	Reference
Grindometer value [μm]	< 10	< 10	< 10	/
Viscosity (millbase) [mPas]				
6 rpm	58	30	26	30
60 rpm	48	43	33	40
Wave scan long wave	4.8	1.2	1.1	1.4
short wave	6.5	3.0	3.1	4.7
20° reflectometer value before scratching	89.0	90.2	89.6	90.8
Haze before scratching	4	4	3	4
40 strokes with Sikron F 500 Residual gloss [%]	78.3	85.9	86.2	55.3

It is shown that a substantially better improvement in the residual gloss is achieved after a scratch stressing of the lacquer surface by using the silicas according to the invention than with the prior art. In addition, owing to

their low rheological efficiency, the silicas according to the invention do not cause an orange-peel effect.

## Claims

1. Silanised, structurally modified, pyrogenically produced silicas, characterised by groups fixed to the surface, wherein the groups are dimethylsilyl and/or monomethylsilyl.
2. Silanised, structurally modified, pyrogenically produced silicas according to claim 1, characterised by the following physico-chemical characteristics:

BET surface area m <sup>2</sup> /g:	25 - 400
Average size of the primary particles nm:	5 - 50
pH value:	3 - 10
Carbon content %:	0.1 - 10
DBP value %:	< 200
3. Process for the production of the silanised, structurally modified, pyrogenically produced silica according to claim 1, characterised in that pyrogenically produced silica is treated by a known method with dimethyldichlorosilane and/or monomethyltrichlorosilane, the groups dimethylsilyl and/or monomethylsilyl being fixed on the surface of the pyrogenic silica, and is then structurally modified and optionally post-ground.
4. Process for the production of the silanised, structurally modified, pyrogenically produced silica according to claim 3, characterised in that a tempering takes place after the structural modification and/or post-grinding.
5. Use of the silanised, structurally modified, pyrogenically produced silica to improve the scratch resistance of lacquers.

## INTERNATIONAL SEARCH REPORT

International Application No

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A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 C09C1/30 C09D7/12

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09C C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 020 419 A (JONSCHKER GERHARD ET AL) 1 February 2000 (2000-02-01) cited in the application column 3, line 57 - line 67 ---	1,5
X	US 6 316 050 B1 (HENNIG THOMAS ET AL) 13 November 2001 (2001-11-13) column 1, line 34 - line 63 column 3, line 12 - line 14 examples; tables ---	1,2
X	US 4 015 031 A (REINHARDT HELMUT ET AL) 29 March 1977 (1977-03-29) claims ---	1
X	US 5 959 005 A (HENNIG THOMAS ET AL) 28 September 1999 (1999-09-28) the whole document --- -/--	1-3



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents:

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Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

International Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01 64796 A (FERON ALUMINIUM ;FERON BERTHOLD (DE); HIRT KLAUS (DE); HOELS LOTHA) 7 September 2001 (2001-09-07) the whole document -----	5

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Information on patent family members

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